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(54) ELECTRIC DOUBLE-LAYER CAPACITOR USING HIGH MOLECULAR SOLID ELECTROLYTE

(57) Abstract:

PURPOSE: To provide an electric double-layer capacitor in which there is no leakage of liquid and which has a capacitance almost equal to that of the system using an electrolyte by using a high molecular solid electrolyte with a high conductivity by which an electrolytic salt such as alkylammonium, etc., can be dissolved sufficiently.

CONSTITUTION: An aprotic solvent as a plasticizer is added to a polyacrylonitrile or a polyethylene oxide-graft polymethacryl acid, and further, as an electrolytic salt, a tetraacrylammonium salt is added thereto to make a high molecular film complex. The complex is used for the high molecular solid electrolyte of an electric double-layer capacitor which has contacting polarization electrodes. Therefore, by using the high-molecular solid electrolyte exhibiting a high conductivity in case where various kinds of tetraarylammonium salts are used, there is no fear of leaking of liquid and the system having a capacitance almost equal to that of the same kind of capacitor containing an electrolyte can be constructed.

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CLAIMS

[Claim(s)]

[Claim 1]A solid polymer electrolyte electric double layer capacitor containing an organic solvent as electrolyte salt and a plasticizer which consists of a polarizable electrode opposite-**(ed) by both sides of a solid polymer electrolyte.

[Claim 2]A solid polymer electrolyte electric double layer capacitor given in the 1st paragraph of a claim which said electrolyte salt becomes from tetraethylammonium tetrafluoroborate, tetraethylammonium perchlorate, or tetrabutylammonium perchlorate.

[Claim 3]A solid polymer electrolyte electric double layer capacitor given in the 1st paragraph of a claim which nonprotic solvents, such as ethylene carbonate, propylene carbonate, sulfolane, and gamma-butyrolactone, were independently used for said plasticizer, respectively, or mixed and used two sorts of plasticizers of these.

[Claim 4]A solid polymer electrolyte electric double layer capacitor given in the 1st paragraph of a claim for which said solid polymer electrolyte used polyacrylonitrile or polyethylene oxide graft poly methyl methacrylate.

[Claim 5]A solid polymer electrolyte electric double layer capacitor given in the 1st paragraph of a claim which consists of an electrode material in which said polarizable electrode made a subject blanket-like carbon materials, such as a carbon nonwoven fabric or an activated carbon-ized carbon nonwoven fabric.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a solid polymer electrolyte electric double layer capacitor. This solid polymer electrolyte electric double layer capacitor has the characteristic of having used the electric double layer formed in the interface of a polarizable electrode and an electrolyte and that electric capacity is large. This considers it as the object for backup of a computer memory, or the auxiliary power of a cell, and is used.

It is used combining the rechargeable battery of high energy density as a power supply of an electromobile.

[0002]

[Description of the Prior Art]The thing using the thing which this old kind of electric double layer capacitor made dissolve the alkyl ammonium salt as electrolyte salt in organic solvents, such as gamma-butyrolactone, as an electrolysis solution is known. This alkyl ammonium salt is a suitable substance for the purpose of it being electrochemically stable and storing up an electric charge in the electric double layer formed by physical adsorption of the electrolyte salt to an electrode surface.

Therefore, it was a conventional method which it is considered as the organic solvent in which such electrolyte salt is made to dissolve enough, and an electrolyte is dissolved using gamma-butyrolactone etc., and is used as an electrolysis solution. However, since the electrolysis solution of the fluid is used, there is fear of liquid leakage on the occasion of long-term use, in order to establish long term reliability, the structure for cheating out of a seal thoroughly is needed, and the conventional electric double layer capacitor brings a result in which the weight itself increases.

[0003]Although it replaces with organic electrolysis liquid, and is made to the structure where liquid leakage does not happen by using a solid electrolyte and it is thought that a separator moreover also becomes unnecessary, Electrolyte salt, such as alkyl ammonium salt, could fully be dissolved, and selecting the solid polymer electrolyte in which high conductivity is moreover shown had a difficulty.

[0004]

[Problem(s) to be Solved by the Invention]By the purpose of this invention fully being able to dissolve electrolyte salt, such as alkyl ammonium salt, creating the solid polymer electrolyte in which high conductivity is moreover shown, and using this, It is providing a solid polymer electrolyte electric double layer capacitor with the capacity which is moreover equal to the electric double layer capacitor using an electrolysis

solution by there being no liquid leakage, and structure becoming easy since it is not necessary to use a separator.

[0005]

[Means for Solving the Problem] This invention to polyacrylonitrile or polyethylene oxide graft polymethacrylic acid. Use ethylene carbonate, propylene carbonate, sulfolane, and gamma-butyrolactone independently as a plasticizer, respectively, or mix and use two sorts of plasticizers of these, and further as electrolyte salt, A poly membrane complex produced by adding tetraethylammonium tetrafluoroborate, tetraethylammonium perchlorate, or tetrabutylammonium perchlorate is used for a solid polymer electrolyte of a electric double layer capacitor.

[0006]

[Function] The poly membrane complex in this invention could dissolve uniformly the electrolyte salt of the concentration which is equal to an electrolysis solution, it became clear that a liquid component did not leak, and it was checked that high conductivity is shown at a room temperature. When it furthermore inserted by two electrodes using these poly membrane complex as a carbon material nonwoven fabric and the characteristic as a capacitor was examined, in the charge-and-discharge capacity test between the between potential 1V and 2V, the performance which is equal to the capacitor using an electrolysis solution was shown very much.

[0007]

[Comparative example 1] dissolving tetraethyl fluoroborate as electrolyte salt in volume ratio 1:1 mixed solution of ethylene carbonate and sulfolane by $0.8\text{mol}\text{dm}^{-3}$ concentration, and measuring conductivity -- a place -- 298K -- $4\times 10^{-3}\text{Scm}^{-1}$ -- conductivity was obtained. This electrolysis solution was inserted into the activated carbon nonwoven fabric by two electrodes which made the nickel network weld as a charge collector, and when the charge and discharge test was done very much with 1V and 1 mA of current from the between potential 2V, the capacity of 0.40Fcm^{-2} was obtained to the apparent electrode surface product at the first time.

[0008]

[Work example 1] 10 ml of plasticizer solutions which dissolved 0.44g of electrolyte salt in 0.88 g of polyacrylonitrile were mixed. This fluid was dried under 393K and 40mmHg decompression for 2 hours, and the poly membrane complex was obtained by neglecting it in a 2 more hour vacuum. A series of operations were performed under dry argon atmosphere. When propylene carbonate was used for the plasticizer here, using tetraethylammonium tetrafluoroborate as electrolyte salt, the poly membrane complex showed the conductivity of $4\times 10^{-3}\text{Scm}^{-1}$ by 298K. This was inserted into the activated carbon nonwoven fabric by two electrodes which made the nickel network weld as a charge collector, and when the charge and discharge test was done very much with 1V and 1 mA of current from the between potential 2V, the capacity of 0.60Fcm^{-2} was obtained to the apparent electrode surface product at the first time. This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0009]

[Work example 2] Methoxy poly(ethylene glycol) mono- methacrylate and poly (ethylene glycol) dimethacrylate are mixed by the mole ratio 3:1 as a prepolymer of the purpose polymers, The plasticizer solution which dissolved electrolyte salt by $0.8\text{mol}\text{dm}^{-3}$ concentration was mixed by the volume ratio 1:1 to the prepolymer mixed solution. Furthermore, a small amount of 2 and 2-dimethoxy- 2-phenylacetophenones were added here

as a photopolymerization initiator, the ultraviolet radiation exposure was performed, and the poly membrane complex was obtained. A series of operations were performed under dry argon atmosphere. When volume ratio 1:1 mixed solution of ethylene carbonate and sulfolane was used for the plasticizer solution here, using tetraethylammonium tetrafluoroborate as electrolyte salt, the poly membrane complex showed the conductivity of $9 \times 10^{-4} \text{ Scm}^{-1}$ by 298K. This was inserted into the activated carbon nonwoven fabric by two electrodes which made the nickel network weld as a charge collector, and when the charge and discharge test was done very much with 1V and 1 mA of current from the between potential 2V, the capacity of 0.38 Fcm^{-2} was obtained to the apparent electrode surface product at the first time. This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0010]

[Work example 3]The method of Example 2 estimated preparation and the characteristic for the poly membrane complex. However, tetraethylammonium perchlorate was used as electrolyte salt here. In this case, the conductivity in 298K was $6 \times 10^{-4} \text{ Scm}^{-1}$. The capacity as a capacitor was 0.30 Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0011]

[Work example 4]The method of Example 2 estimated preparation and the characteristic for the poly membrane complex. However, tetrabutylammonium perchlorate was used as electrolyte salt here. In this case, the conductivity in 298K was $5 \times 10^{-4} \text{ Scm}^{-1}$. The capacity as a capacitor was 0.06 Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0012]

[Work example 5]The method of Example 2 estimated preparation and the characteristic for the poly membrane complex. However, propylene carbonate was used as a plasticizer here, using tetraethylammonium tetrafluoroborate as electrolyte salt. In this case, the conductivity in 298K was $3 \times 10^{-3} \text{ Scm}^{-1}$. The capacity as a capacitor was 0.42 Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0013]

[Work example 6]The method of Example 2 estimated preparation and the characteristic for the poly membrane complex. However, propylene carbonate was used as a plasticizer here, using tetraethylammonium perchlorate as electrolyte salt. In this case, the conductivity in 298K was $2 \times 10^{-3} \text{ Scm}^{-1}$. The capacity as a capacitor was 0.31 Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0014]

[Work example 7]The method of Example 2 estimated preparation and the characteristic for the poly membrane complex. However, propylene carbonate was used as a plasticizer here, using tetrabutylammonium perchlorate as electrolyte salt. In this case, the conductivity in 298K was $1 \times 10^{-3} \text{ Scm}^{-1}$. The capacity as a capacitor was 0.21 Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0015]

[Work example 8]Preparation and the characteristic were evaluated for the poly membrane complex mentioned as Example 5. However, in the capacity test as a capacitor, current was 0.5 mA here. In this case, capacity was 0.60Fcm^{-2} . This poly membrane complex was flexible, and before and after doing a charge and discharge test, in any, the break through of the liquid component was not seen at all.

[0016]

[Effect of the Invention]As mentioned above, it became clear that a system with the capacity which is equal to a capacitor with an electrolysis solution of the same kind could be built by using for the electrolyte of a electric double layer capacitor the solid polymer electrolyte in which high conductivity is shown when various tetra-alkyl ammonium salt is used. As mentioned to the example, as electrolyte salt, it turned out as tetrafluoroborate and a plasticizer that propylene carbonate is more desirable. When the current density for charge and discharge was low, it also turned out that capacity increases more. Since these capacitors do not have fear of liquid leakage, the reliability for long-term use is high, and the effect is large.

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TECHNICAL FIELD

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TECHNICAL PROBLEM

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MEANS

[Means for Solving the Problem]This invention to polyacrylonitrile or polyethylene oxide graft polymethacrylic acid. Use ethylene carbonate, propylene carbonate, sulfolane, and gamma-butyrolactone independently as a plasticizer, respectively, or mix and use two sorts of plasticizers of these, and further as electrolyte salt, A poly membrane complex produced by adding tetraethylammonium tetrafluoroborate, tetraethylammonium perchlorate, or tetrabutylammonium perchlorate is used for a solid polymer electrolyte of a electric double layer capacitor.

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OPERATION

[Function]The poly membrane complex in this invention could dissolve uniformly the electrolyte salt of the concentration which is equal to an electrolysis solution, it became clear that a liquid component did not leak, and it was checked that high conductivity is shown at a room temperature. When it furthermore inserted by two electrodes using these poly membrane complex as a carbon material nonwoven fabric and the characteristic as a capacitor was examined, in the charge-and-discharge capacity test between the between potential 1V and 2V, the performance which is equal to the capacitor using an electrolysis solution was shown very much.

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最終頁に続く

(54)【発明の名称】 高分子固体電解質電気二重層コンデンサー

(57)【要約】

【目的】 アルキルアンモニウム塩などの電解質塩を充分に溶解させることができ、しかも高い導電性を示す高分子固体電解質を用いることにより、液漏れがなく、しかも電解液を用いた系に匹敵する容量を持つ電気二重層コンデンサーを提供する。

【構成】 ポリアクリロニトリル、またはポリエチレンオキシドーグラフトポリメタクリル酸に、可塑剤として非プロトン溶媒を加え、さらに電解質塩として、テトラアルキルアンモニウム塩を加えた高分子膜複合体を、対接された分極性電極を持つ電気二重層コンデンサーの高分子固体電解質に用いる。

【効果】 各種テトラアルキルアンモニウム塩を用いた場合に高い伝導性を示す高分子固体電解質を、電気二重層コンデンサーに用いる事により、液漏れの恐れがなく、電解液を持つ同種のコンデンサーに匹敵する容量を持つ系が構築できた。

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【特許請求の範囲】

【請求項1】電解質塩ならびに可塑剤としての有機溶媒を含む、高分子固体電解質の両面に対接された分極性電極からなる高分子固体電解質電気二重層コンデンサー。

【請求項2】前記電解質塩は、テトラエチルアンモニウムテトラフルオロボレート、テトラエチルアンモニウムバーコロレート、またはテトラブチルアンモニウムバーコロレートからなる請求項第1項記載の高分子固体電解質電気二重層コンデンサー。

【請求項3】前記可塑剤は、エチレンカーボネート、アロビレンカーボネート、スルホラン、アーブチロラクトン等の非プロトン溶媒をそれぞれ単独で用いるか、あるいはこのうちの二種の可塑剤を混合して用いた請求項第1項記載の高分子固体電解質電気二重層コンデンサー。

【請求項4】前記高分子固体電解質は、ポリアクリロニトリル、またはポリエチレンオキシドーグラフトポリメタクリル酸メチルを用いた請求項第1項記載の高分子固体電解質電気二重層コンデンサー。

【請求項5】前記分極性電極は、カーボン不織布もしくは活性炭化カーボン不織布等の布状カーボン材料を主体とした電極材料からなる請求項第1項記載の高分子固体電解質電気二重層コンデンサー。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は高分子固体電解質電気二重層コンデンサーに関するものである。この高分子固体電解質電気二重層コンデンサーは、分極性電極と電解質との界面に形成される電気二重層を利用して静電容量の大きい特性を有するものである。これは、コンピューターメモリーのバックアップ用、あるいは電池の補助電源、として用いられるものであり、また電気自動車の電源として高エネルギー密度の二次電池と組み合わせて用いられるものである。

【0002】

【従来の技術】これまでのこの種の電気二重層コンデンサーは、電解質塩としてのアルキルアンモニウム塩をアーブチロラクトンなどの有機溶媒に溶解させたものを電解液として用いたものが知られている。このアルキルアンモニウム塩は、電気化学的に安定であり、電極表面への電解質塩の物理的吸着により形成される電気二重層に電荷を蓄積させるという目的には好適の物質である。従って、これらの電解質塩を充分溶解せしめる有機溶媒としてアーブチロラクトン等を用い、電解質を溶解させ電解液として使用するのが常法であった。しかしながら、従来の電気二重層コンデンサーは液体の電解液を用いているため、長期使用に際しては液漏れの恐れがあり、長期信頼性を確立するためにはシールを完全にせしめるための構造が必要となり、重量自身も増大する結果となる。

【0003】有機電解液に代えて、固体電解質を用いる

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ことにより液漏れが起らぬ構造にでき、しかもセパレーターも不要になると考えられるが、アルキルアンモニウム塩などの電解質塩を充分に溶解させることができ、しかも高い導電性を示す高分子固体電解質を選定することに難点があった。

【0004】

【発明が解決しようとする課題】本発明の目的は、アルキルアンモニウム塩などの電解質塩を充分に溶解させることができ、しかも高い導電性を示す高分子固体電解質を作成し、これを用いることにより、液漏れがなく、セパレーターを用いる必要がないため構造が簡単になり、しかも電解液を用いた電気二重層コンデンサーに匹敵する容量を持つ高分子固体電解質電気二重層コンデンサーを提供することである。

【0005】

【課題を解決するための手段】本発明は、ポリアクリロニトリル、またはポリエチレンオキシドーグラフトポリメタクリル酸に、可塑剤としてエチレンカーボネート、アロビレンカーボネート、スルホラン、アーブチロラクトンをそれぞれ単独で用いるか、あるいはこのうちの二種の可塑剤を混合して用い、さらに電解質塩として、テトラエチルアンモニウムテトラフルオロボレート、テトラブチルアンモニウムバーコロレート、またはテトラブチルアンモニウムバーコロレートを加えて得られた高分子膜複合体を、電気二重層コンデンサーの高分子固体電解質に用いるものである。

【0006】

【作用】本発明における高分子膜複合体は、電解液に匹敵する濃度の電解質塩を均一に溶解でき、液体成分が漏れないことが判明し、室温で高い導電性を示すことが確認された。さらにこれら高分子膜複合体をカーボン材料不織布として用いた電極二枚によりはさみ、コンデンサーとしての特性を検討したところ、極間電位1Vと2V間での充放電容量試験において、電解液を用いたコンデンサーに匹敵する性能を示した。

【0007】

【比較例1】電解質塩としてのテトラエチルフルオロボレートを 0.8 mol dm^{-3} 濃度でエチレンカーボネートとスルホランの体積比1:1混合溶液に溶解し、伝導度を測定したところ、298Kで $4 \times 10^{-3}\text{ S cm}^{-1}$ の伝導度を得た。この電解液を活性炭不織布にニッケル網を集電体として溶着させた電極二枚ではさみ、極間電位2Vから1V、電流1mAで充放電試験を行ったところ、初回でみかけの電極表面積にたいし、0.40 F cm⁻²の容量が得られた。

【0008】

【実施例1】ポリアクリロニトリル0.88gに、電解質塩を0.44g溶解した可塑剤溶液10mLを混合した。この液体を393K、40mmHg減圧下で2時間乾燥させ、さらに2時間真空中で放置することにより高

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分子膜複合体を得た。なお、一連の操作は乾燥アルゴン雰囲気下で行った。ここで電解質塩としてテトラエチルアンモニウムテトラフルオロボレートを用い、可塑剤にプロピレンカーボネートを用いると、高分子膜複合体は298Kで $4 \times 10^{-3} \text{ S cm}^{-1}$ の伝導度を示した。これを活性炭不織布にニッケル網を集電体として溶着させた電極二枚ではさみ、極間電位2Vから1V、電流1mAで充放電試験を行ったところ、初回でみかけの電極表面積にたいし、 0.60 F cm^{-2} の容量が得られた。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0009】

【実施例2】目的高分子のプレポリマーとしてメトキシポリ(エチレングリコール)モノメタクリレートとポリ(エチレングリコール)ジメタクリレートをモル比3:1で混合し、電解質塩を 0.8 mol dm^{-3} 濃度で溶解した可塑剤溶液をプレポリマー混合溶液に体積比1:1で混合した。さらにここに光重合開始剤として2,2-ジメトキシ-2-フェニルアセトフェノンを少量加え、紫外光照射を行い、高分子膜複合体を得た。なお、一連の操作は乾燥アルゴン雰囲気下で行った。ここで電解質塩としてテトラエチルアンモニウムテトラフルオロボレートを用い、可塑剤溶液にエチレンカーボネートとスルホランの体積比1:1混合溶液を用いると、高分子膜複合体は298Kで $9 \times 10^{-4} \text{ S cm}^{-1}$ の伝導度を示した。これを活性炭不織布にニッケル網を集電体として溶着させた電極二枚ではさみ、極間電位2Vから1V、電流1mAで充放電試験を行ったところ、初回でみかけの電極表面積にたいし、 0.38 F cm^{-2} の容量が得られた。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0010】

【実施例3】実施例2の方法で高分子膜複合体を調製、ならびに特性を評価した。但しここでは電解質塩としてテトラエチルアンモニウムバーカロレートを用いた。この場合、298Kにおける伝導度は $6 \times 10^{-4} \text{ S cm}^{-1}$ であった。コンデンサーとしての容量は 0.30 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0011】

【実施例4】実施例2の方法で高分子膜複合体を調製、ならびに特性を評価した。但しここでは電解質塩としてテトラブチルアンモニウムバーカロレートを用いた。この場合、298Kにおける伝導度は $5 \times 10^{-4} \text{ S cm}^{-1}$ であった。コンデンサーとしての容量は 0.06 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液

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体成分の漏出は何ら見られなかった。

【0012】

【実施例5】実施例2の方法で高分子膜複合体を調製、ならびに特性を評価した。但しここでは電解質塩としてテトラエチルアンモニウムテトラフルオロボレートを用い、可塑剤としてプロピレンカーボネートを用いた。この場合、298Kにおける伝導度は $3 \times 10^{-3} \text{ S cm}^{-1}$ であった。コンデンサーとしての容量は 0.42 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0013】

【実施例6】実施例2の方法で高分子膜複合体を調製、ならびに特性を評価した。但しここでは電解質塩としてテトラエチルアンモニウムバーカロレートを用い、可塑剤としてプロピレンカーボネートを用いた。この場合、298Kにおける伝導度は $2 \times 10^{-3} \text{ S cm}^{-1}$ であった。コンデンサーとしての容量は 0.31 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0014】

【実施例7】実施例2の方法で高分子膜複合体を調製、ならびに特性を評価した。但しここでは電解質塩としてテトラブチルアンモニウムバーカロレートを用い、可塑剤としてプロピレンカーボネートを用いた。この場合、298Kにおける伝導度は $1 \times 10^{-3} \text{ S cm}^{-1}$ であった。コンデンサーとしての容量は 0.21 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0015】

【実施例8】実施例4に挙げた高分子膜複合体を調製、ならびに特性を評価した。但しここではコンデンサーとしての容量試験において電流を0.5mAとした。この場合、容量は 0.60 F cm^{-2} であった。この高分子膜複合体は、フレキシブルであり、充放電試験を行う前後いずれにおいても、液体成分の漏出は何ら見られなかった。

【0016】

【発明の効果】以上のように、各種テトラアルキルアンモニウム塩を用いた場合に高い伝導性を示す高分子固体電解質を、電気二重層コンデンサーの電解質に用いる事により、電解液を持つ同種のコンデンサーに匹敵する容量を持つ系が構築できる事が判明した。実施例に挙げたように電解質としてはテトラフルオロボレート、可塑剤としては、プロピレンカーボネートがより望ましい事がわかった。また、充放電に際しての電流密度が低いと容量がより増大する事もわかった。これらのコンデンサーは液漏れの恐れがないため、長期使用に際しての信頼

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性が高く、その効果は大きい。

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